"Nanocrystalline Processing and Interface Engineering of Si_3N_4-based Ceramics"

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Jackie Y. Ying
Cabot Assistant Professor
Department of Chemical Engineering
Massachusetts Institute of Technology
Room 66-544, 25 Ames Street
Cambridge, MA 02139
Tel: (617) 253-2899
FAX: (617) 258-8224

Our efforts over the last three months have been focused on doing preliminary set-up work vital for future success on this research project. Several key components were designed and added to the tubular flow reactor, used in the synthesis of our nanocrystalline Si_3N_4, and two pieces of equipment used for processing our material, a sintering furnace and a hot press, were designed and constructed.

Construction of the novel tubular flow reactor for the synthesis of nanocrystalline materials by thermal evaporation in a forced flux of gas is nearly complete. The reactor was modified to accommodate a second gas entrance just beyond the evaporation source. The original gas entrance is used to introduce helium for the evaporation and to carry the silicon particles just beyond the evaporation crucible. The second gas entrance is used to introduce nitrogen to then nitride the silicon particles and form Si_3N_4 powder. (If the nitrogen is introduced before the evaporation source, the molten silicon in the crucible is nitrided and Si_3N_4 in the crucible quickly inhibits any further evaporation.) A collection substrate in the form of a rotating, liquid nitrogen cooled stainless steel disc was installed in the collection chamber of the reactor. This disc collects the nanocrystalline Si_3N_4 powder by thermophoresis. As the plate is oriented parallel to the flow of the carrier gases, the plate faces where powder collection takes place are not heated and collection remains efficient for extended periods of time. A sample loader, used to continually replenish the supply of the material being evaporated (i.e. raw silicon in our production of Si_3N_4), was added to the evaporation chamber of the reactor. A magnetically coupled transfer device allows silicon to be continuously transported from a reservoir at the front of the reactor into the evaporation boat. Finally, the transformers used to power the evaporation source were replaced with new transformers which will allow the use of both tungsten (a high amperage/low voltage) and carbon (low amperage/high voltage) based evaporation boats. The carbon/graphite boats are more resistive to silicon alloying than are the tungsten boats and longer evaporation times without crucible failure should be achieved. Surface treatments of the carbon crucibles are being explored to impede the formation of silicon carbide during reactor operation. As part of this transformer modification, vacuum and cooling water safety interlocks were added to allow the reactor to safely operate continuously for long periods of time. A schematic of the tubular flow reactor is shown in Figure 1.

The first experiments using the reactor involved the evaporation of silicon in a helium atmosphere in the evaporation chamber. A liquid nitrogen cooled cold finger was inserted into the top of the evaporation chamber for sample collection. (The rest of the reactor was isolated separately from the evaporation chamber for these experiments. This procedure also allowed leak-checking of the reactor to take place.) Evaporation

experiments to determine the optimal operating pressure were performed between 0.5 mbar and 11 mbar. A TEM micrograph illustrates that particles produced at 0.5 mbar (Figure 2a) are sized between 10 and 15 nanometers (well within our desired range). As shown in Figure 2b, a pressure of 11 mbar is too high and leads to the formation of long, aggregated chains of particles. Through these preliminary experiments, much valuable information regarding operating pressures, molten silicon behavior and reactor performance was obtained. Our next step is to nitride the Si particles using the full length of the tubular reactor and examine the effects of gas flow rates on particle size distribution, morphology and collection yield.

Once large quantities of nanocrystalline Si_3N_4 are produced, the processing routes of both pressureless sintering and sinter-forging will be examined. Design and construction of the equipment required is complete. A Lindberg 1700 °C tube furnace was modified with a temperature and atmosphere control system. The furnace tube, sealed with a pair of custom built water-cooled vacuum end caps that allow quick access to the furnace, can be filled with any gas atmosphere desired. A programmable temperature controller wired to the furnace allows the required ramp and soak cycles for pressureless sintering to 1700 °C to be performed.

The sinter-forging/hot press apparatus was built to our specifications by Materials Research Furnaces (MRF). We worked with their engineers to design an apparatus that can hot press/sinter-forge material with 10,000 lbs of load at temperatures up to 2000 °C. The equipment can operate in an inert gas or vacuum atmosphere. The hot press was delivered to us on June 20th. Installation and training should be completed within the next two weeks. The equipment is shown in Figure 3.

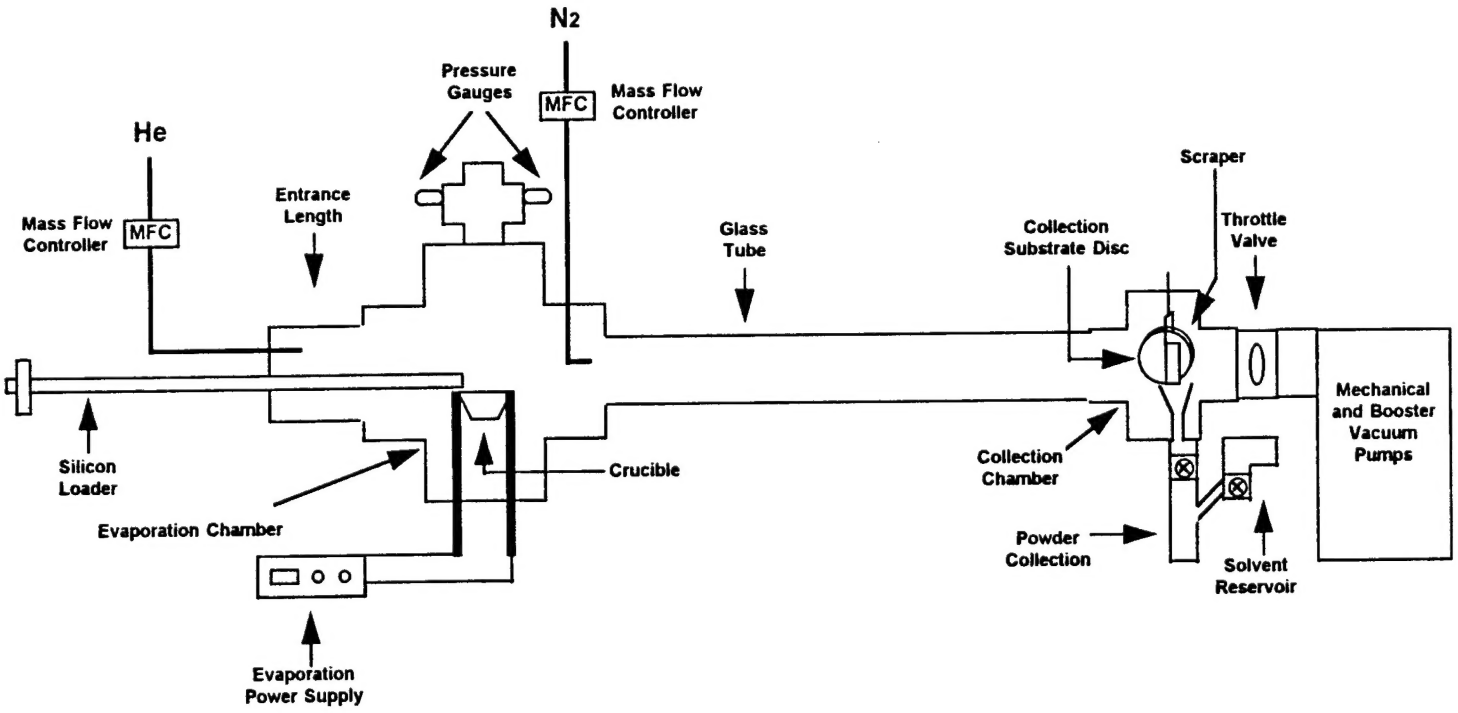

Figure 1: Schematic of tubular flow reactor [1]

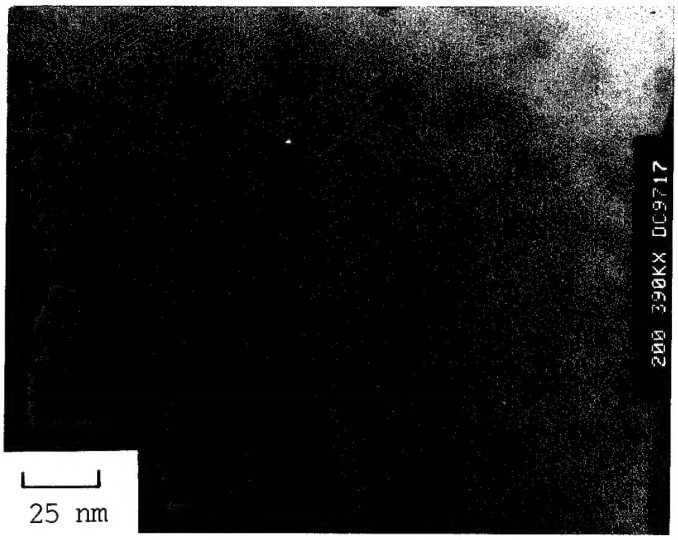

Figure 2a: Si nanoclusters P = 0.5 mbar
Magnification = 390000x [1]

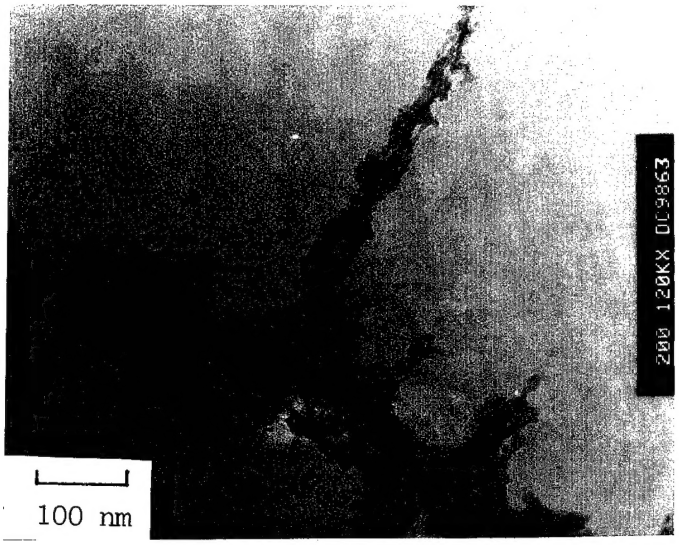

Figure 2b: Si nanoclusters P = 11 mbar
Magnification = 120000x [1]

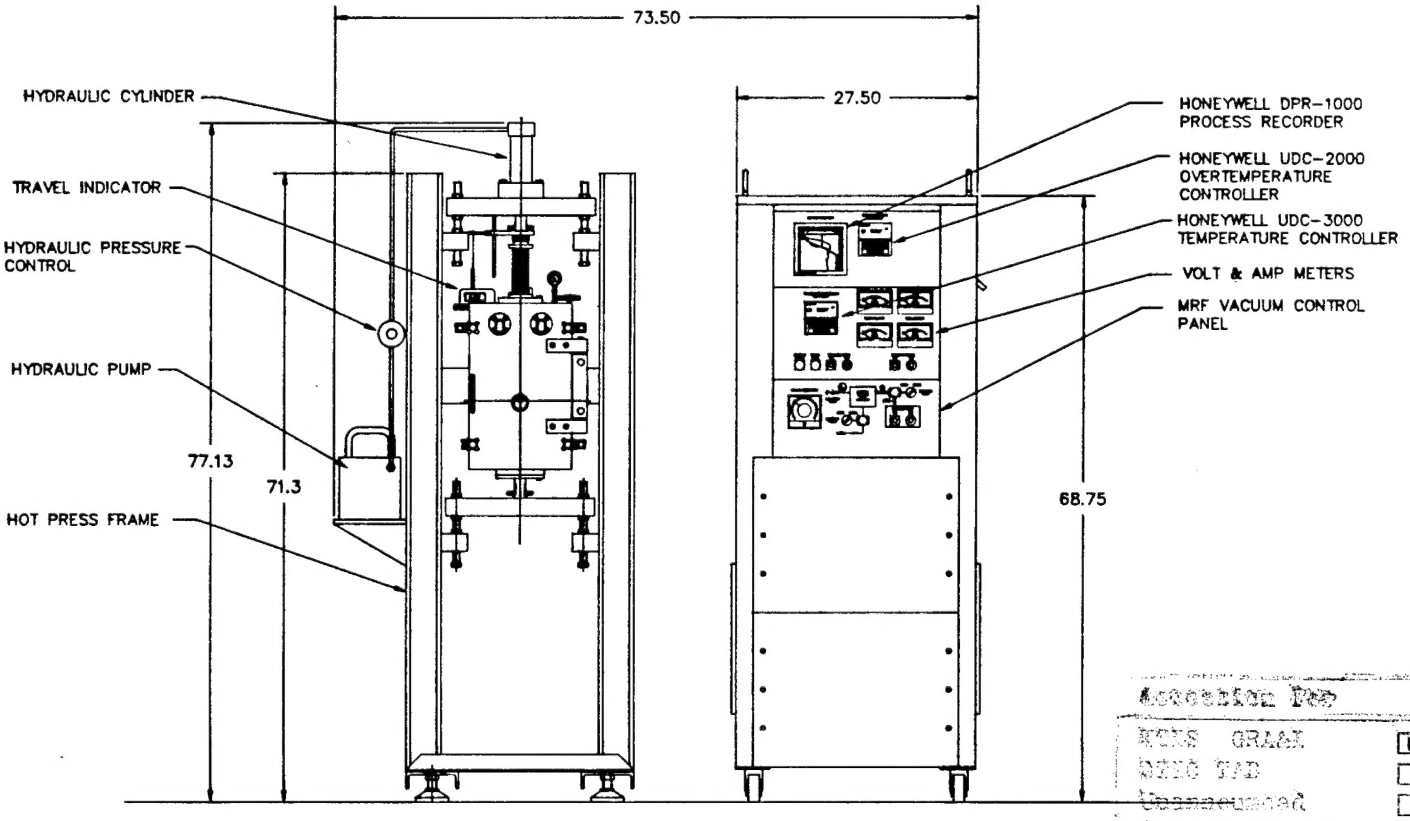

Figure 3: Hot press/sinter-forge apparatus

Reference

[1] D.T. Castro and J.Y. Ying, to be submitted.